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" Electronic Processes at Grain Boundaries ".

Investigations of electronic phenomena occuring at intercrystalline boundaries have been carried on, for some time, in our laboratory in Warsaw.* I had alrеdy an opportunity to present some of the results at recent Brussel Conference(1); since however they are not yet published, I shall have to repeat them shortly here.

The work has been carried on silicon and germanium of both n and p types. Samples were prepared either by growing of crystals from a proper seed or by zone melting of an initially single crystal. In this way one obtains twin crystals containing low angle and high angle boundaries. Samples of regular form / usually 10 × 2 × 0,5 mm / were cut from such crystals with a boundary perpendicular to the longest dimension of a sample. The boundaries were made visible under optical or electonmicroskope by proper etching; crystallographical orientation of both parts of the bicrystal established by X - rays diffraction methods.

The occurance of two kinds of boundaries, of essentially different electronic properties was found. We shall call them further the boundaries of the I -st and the II -nd type.

* The work on electronic properties of G B in Ge has been carried on by T. Figielski, extended to Si by M. Jastrzebska; X-rays study of G B - J. Auleytner and M. Lefeld; technological group W. Giriat /Ge/ and T. Niemyski /Si/.

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I -st type correspond to low angle dislocation boundaries; II -nd to high angle boundaries and uncoherent twins.

The boundaries of the I -st kind act as regions of enhanced recombination. This behaviour of G B was observed by many authors / Vogl, Read and Lovell (1) /. The diffusion curve shows a sudden drop at the boundary, when measured in the direction perpendicular to the boundary. Along the boundary one observes a marked decrease in the diffusion length. Typical case is shown in fig 1.

Assuming that surface recombination at G B equal S, and putting α_1 and α_2 for angles of inclinations of tangents to the diffusion curve at the G B, the boundary condition takes form: $tg\,\alpha_1 - tg\,\alpha_2 = S'/D$

Due however to finite dimension of a generating light spot, this angles could not be well measured directly. Solving diffusion equation: $\frac{\partial^2 p}{\partial x^2} - \frac{p}{L^2} = 0$, with the above boundary conditions, and putting $\log K = \log p_{1e} - \log p_{2e}$, where p_{1e} and p_{2e} are values at the boundary of extrapolated linear parts of the diffusion curve, one obtains: $S'/D = \frac{2K-1}{L_1} - \frac{1}{L_2}$; K, L_1 and L_2 could be read directly from the graph.

The values of S are the order of 10^3 cm/s; for instance for the case shown in fig 1 $S' = 790$ cm/s.

The boundaries of the II -nd type which properties are the main subject of the present paper, show a number of striking and rather unexpected features.

Their main properties are as follows:

1. Occurence of photo - emf when boundary is assymetrically illuminated.(3) This photo - emf changes its sign when the light spot crosses the boundary / for n -type, the illuminated part of the bicrystal charges negatively, for p -type postively/(3). /fig 2/

2. Fotoconductivity of a sample shows a pronounced peak when the light spot crosses the boundary. The slope of logarithm of photocurrent vs. distance from the boundary curve corresponds to the diffusion length of the minority carriers /fig 3/.

3. Transverse diffusion curve shows deviations from a regular behaviour;(4,5) near the boundary one observes usually a maximum of the collector current /fig.4/. This deviation from a monotonic fall is connected however, with the influence of photo - emf on collector, and can be partly or wholly eliminated by increased collector selectivity for minority carriers or by background illumination of a sample. Corrected diffusion curves do not show any discontinuity at the boundary, thus indicating apparent S=0.

4. Diffusion length measured along or parallel to the boundary is increased above that of the bulk material. This increase may be so marked that the collector current is almost constant over the whole length of the boundary / 1 - 2 mm /.

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Strong background illumination or polarising voltage of few volts applied to the boundary reduces the apparent diffusion length to its normal value /fig.3/.

5. The current - voltage relation for samples containg such boundary is similar to the diode characteristic in blocking direction.

The above mentioned facts lead us to the conclusion of existance at the boundary of an inversion layer i.e. n - p - n junction for a n - type sample, p - n - p for a p - type. We take for further discussion the first case i.e. n - p - n junction.

Let us assume a n - type semiconductor with a potential barrier ~~[illegible]~~ at the boundary of hight ϕ. We put ψ - for an electrostatic potencial, $e\varphi$ - Fermi level, w - width of a boundary region, which we assume is small compared with the diffusion length L. Photo - emf V will depend on separation by the barrier of holes and electrons. Assuming that j_0 is a current of holes produced by light and crossing the boundary, one might obtain V from the equilibrium condition $j_0 + j_+ = j_-$ where j_+ and j_- are the diffusion currents of holes and electrons respectively. After simple calculations one obtains for small illumination:

$$V = \frac{kT}{e} \frac{j_0 w}{D_+ p} \left\{ 1 + b \exp \frac{e}{kT} \left[\ldots \right] \ldots \right\}$$ [illegible]

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where $b = \frac{\mu_e}{\mu_h}$, n - density of electrons in the bulk, of sample and p_b - density of holes in boundary region. From the above formula one can see that appreciable values of V occur only when $p_b \gg n$, i.e. when boundary is of $n - p^+ - n$ type.

As the occurrence of the photo - emf is the most essential feature of G Bs of the II -nd type, we are forced to assume the existance of p^+ region at such boundary. This assumption is sufficient for explaining all other features of this type of G B.

The irregular behaviour of the diffusion curve can be then connected with "feed - in feed - out effect", first noticed by Moore and Webster for $n - p^+$ junctions /6/.

Essential for "feed - in, feed - out effect" /shortly ffo/ is the interaction between the holes by their electrostatic field; the hole entering p^+ region disturbes by its charge the barrier layer potential and thus causes the expulsion from the p^+ region of some other hole. Thus the transfer of holes through the boundary region is in this case essentially not a diffusion process.

Let as assume that the disturbance of barrier hight caused by one hole is equal $-\delta\phi$. In the stationary state ϕ must be of course costant, $\delta\phi$ must be compensated either by an incoming electron or by an outcoming hole. Calculating

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Calculating the diffusion currents of holes and electrons caused by the change of the barrier hight $-\delta\phi$, one obtains for probability of expulsion of a hole: $W_p = \left(1 + b\frac{n}{p_b}\right)^{-1}$. Ffe is effective when $W_p \simeq 1$. As the expression for Wp is identical with the binomial coefficient for the photo-emf, one can see, that both this effects should occur simultaniously. At G B showing photo-emf, ffe should be effective and vice versa. Of course, the recombination of a hole in the boundary region have no influence on a hole current crossing the G B; thus ffe explains immediately the continuity of the transverse diffusion curve.

One can also understand the apparent increase of the longitudinal diffusion length. Let us follow propagation along the boundary region of a small potential disturbance caused by injection of some holes at one point. Problem is analogous to that of a transmission line, with capacity par unit length α, and conductivity ξ. One has also to introduce a damping constant $\varkappa$ accunting for leak of holes from the boundary region to the bulk material. We look than for a stationary solutions of differential equation:

$$\alpha\frac{\partial\varphi}{\partial t} = \xi\frac{\partial^2\varphi}{\partial z^2} - \varkappa\varphi, \quad \text{where } \varphi = \phi - \phi_0$$

is the measure of deviation from equilibrium.

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For stationary state $\frac{\partial \varphi}{\partial t} = 0$ and one obtains solution in the form $\varphi = \varphi_0 e^{-\xi \lambda}$ with $\lambda = \xi / x$. Simple consideration gives: $\varkappa = \frac{\sigma_m}{L}\left(1 + b\frac{n}{p_b}\right)$, where $\sigma_m = e\mu_n p$ means minority conductivity of bulk material. For boundary of the II - nd kind, we are new considering, one may put $1 + b\frac{n}{p_b} \simeq 1$. Then: $\lambda / L = \frac{\sigma_b}{\sigma_m}\frac{w}{L})^{1/2}$, where σ_b means conductivity along boundary layer, and w barrier width.

Putting $\mu_b = x\mu$; $p_b / n = \gamma$ one finally obtains $\frac{\lambda}{L} = \left(x \cdot \gamma \cdot \frac{w}{L}\right)^{1/2}\frac{n}{n_i}$. We do not know the exact values neither of x, nor γ or w. Making however reasonable estimations /$w \sim 100 - 1000\,Å$, $\gamma \sim 100$, $x \sim 1$/ one can easily obtain $\lambda \simeq (10 - 100)L$, which is amply sufficient to account for the observations.

Further informations can be gained from investigations of transient phenomena. Experimental data are shown in fig.6. The square - wave voltage pulses have been applied through ohmic electrodes to a sample containing a boundary of the II -nd type and current through the sample observed on the screen of an oscilloscope. The circuit constants were so adjusted that initial peak of current corresponds to charging of a boundary. Crosses on the graph corresponds to peak value, circles - to ~~region~~ stationary value of a current.

No initial peak appears for low voltages applied to the barrier.

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For voltages in the range of 1 - 20 v the peak follows $V^{1/2}$ low; for voltages of about 100 v it disappears again. The last value of voltage agrees with crossing point of an extrapolated $V^{1/2}$ line with the experimental curve.

Let us estimate the influence of an applied voltage on the charge and potential hight of the boundary layer. Let the density of electrons in surface states be equal $S\ cm^{-2}$, the maximum concentration of holes in the boundary region $p_0\ cm^{-3}$. Then from the solution of the Poisson equation one obtains the relation:

$$\left(\phi - \frac{kT}{e}\right) + \frac{kT}{e}\,\frac{p_0}{n} = \frac{\pi e}{2\varepsilon}\,\frac{S^2}{n}$$

/ ε - dielectric constant /.

We may introduce now the notion of effective concentration of holes per unit area, partly compensating the negative surface charge: $p_{ef} = \int p\,dx \simeq \left(\frac{\varepsilon}{2\pi e n \phi \beta^2}\right)^{1/2} p_0$, where $\beta = \frac{e}{kT}$. Putting $\phi = \frac{\pi e S'^2_{ef}}{2 n \varepsilon}$, and assuming $\frac{kT}{e} p_0 < n\phi$, one obtains $S'_{ef} = S' - p_{ef}$.

One can consider thus, that the barrier hight ϕ depends on total charge eS'_{ef} in the boundary region, equal the difference between the charge of electrons in surface states and the charge of holes in the inversion layer.

To account for the influence of an applied voltage V, we shall consider parabolic potential barrier caused by the effective charge eS_{ef}.

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Let ϕ_0 be the hight of the boundary barrier when external voltage is equal zero, ϕ – when an external voltage equals V; $e s^{0}_{ef}$ and $e s'_{ef}$ – corresponding charge densities. Putting $k^2 = \frac{\pi e}{2 n \varepsilon} s^{2}_{ef}$, we have $\phi = (k - eV/4k)^2$ with $\phi_0 = k_0^2$.

Number of electrons in surface states s is an in creasing function of $\Delta\phi = \phi_0 - \phi$: $s = f(\Delta\phi)$. The exact shape of function f depends on energy spectrum of surface states. For single energy level; $s = n_s f = n_s\left[\exp(E_s - \varphi + \phi)\beta + 1\right]^{-1}$; where n_s is the number of surface states of energy E_s.

For high energy levels one obtains aproximately

$$s = s_0 e^{-\beta\Delta\phi}, \text{ thus: } \phi = \left(k_0 e^{\beta\Delta\phi} - V/4k_0\, e^{-\beta\Delta\phi}\right)^2.$$

According to this formula the dependance of ϕ on V is very slow one; for not too high voltages $\Delta\phi \simeq V/4\beta\phi_0$; for high voltages $\Delta\phi = \frac{1}{2\beta}\log V/2\phi_0$. In this range $k \sim V^{1/2}$ in agreement with our experimental results for the range of 2 – 50 volts. When however the surface states become saturated i.e. $f \simeq 1$, s becomes constant and nearly equal n_s and the barrier hight quickly drops. In this conditions the peak in fig.6 should disappear. From the value of voltage at which the peak disappears we can estimate density of surface states, which for most samples is of the order of magnitude of $10^{11} - 10^{12}\ cm^{-2}$.

Simple assumption of a single energy level of surface states does not seem to account for all observed facts. The experimental data of a dependance of longitudonal diffusion lenght on applied voltage and the current - voltage characteristic of photocurrent show that in the range of 0.5 - 2V the barrier hight lowers also considerably. The photo current - voltage characteristic is shown in fig. 7. One should notice a strong increase of the current at some fairly low voltage / its value changes from sample to sample/. This behaviour of photocurrent indicates that electronic component of a current becomes appreciable at these fairly low voltages, which is possible only when φ decreases by some [illegible] below its initial value. One may hope to obtain from such measurements an energy spectrum ~~for~~ of boundary surface states.

1. [illegible] Figielski, Z. [illegible]owski International Conference on Solid State Physics in Electronics and Telecommunications. Brussels June 1958

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4. H.F. Mataré, Z. Naturforschg. 10a, 640 ([illegible])

5. H.F. Mataré, Z. Naturforschg. 11a, 876 ([illegible])

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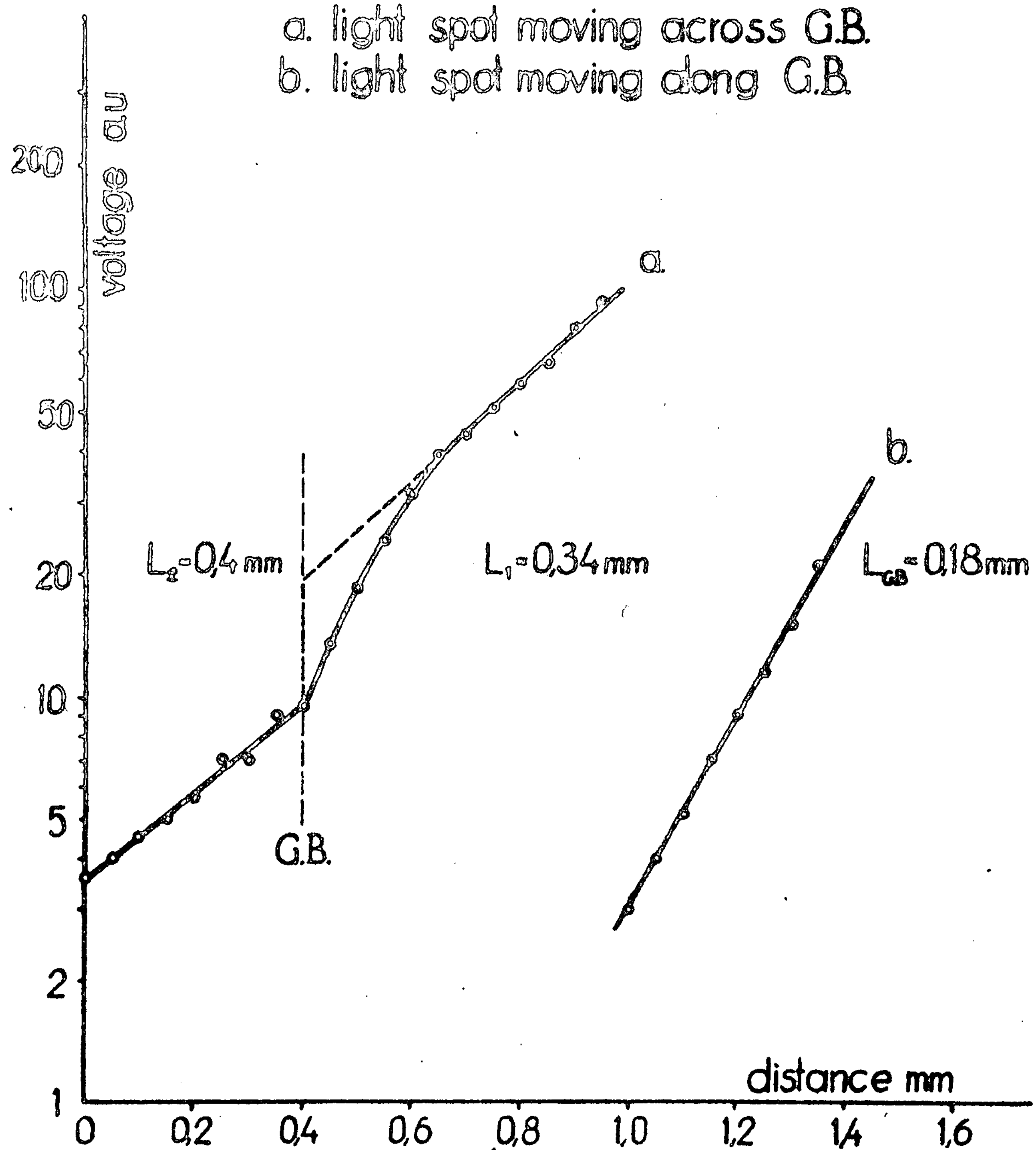
a. light spot moving across G.B.
b. light spot moving along G.B.
voltage a.u
200
100
50
20
10
5
2
1
a.
b.
L_2=0,4 mm
L_1=0,34 mm
L_{GB}=0,18mm
G.B.
distance mm
0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6

Fig.1

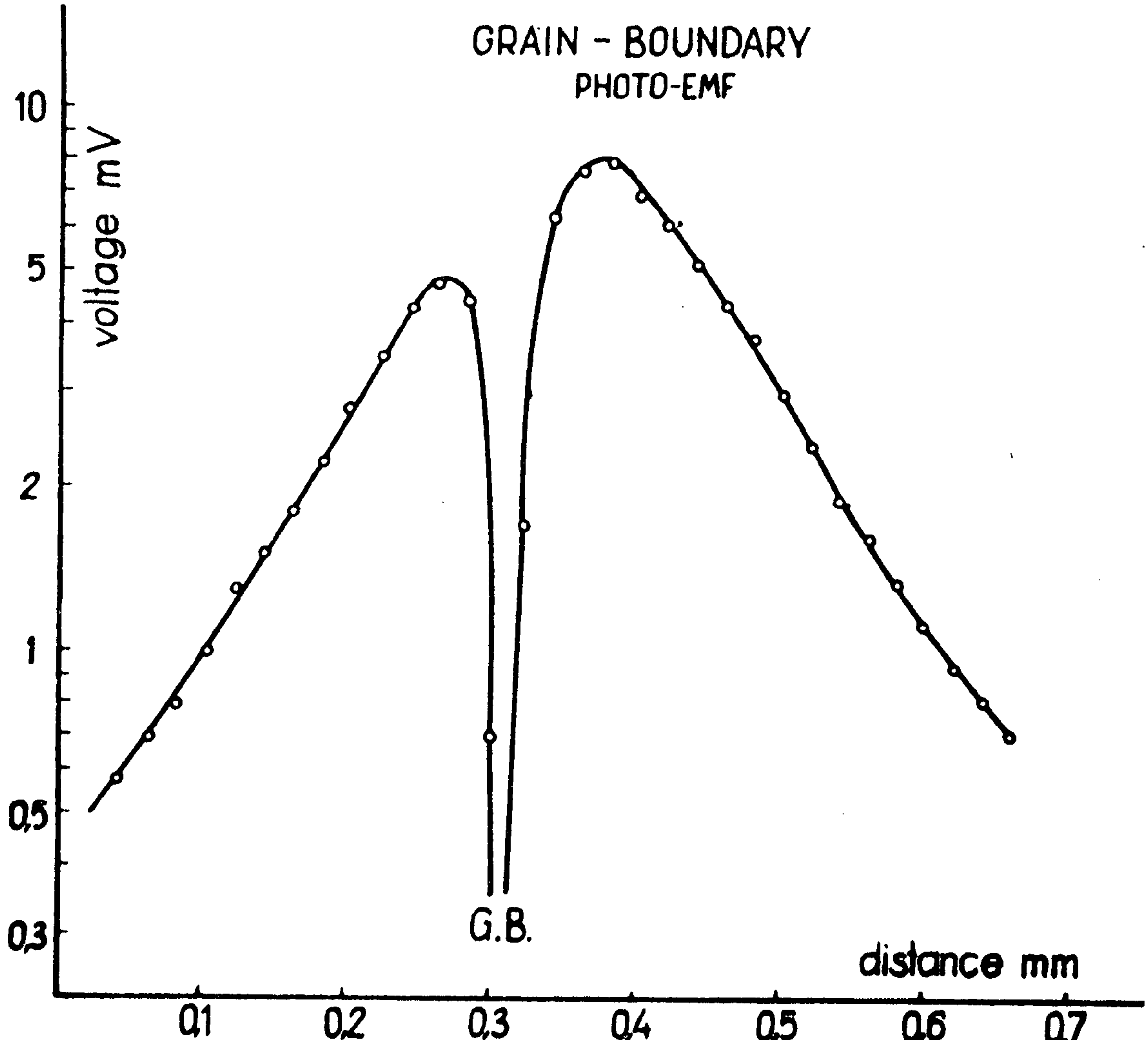
GRAIN - BOUNDARY
PHOTO-EMF
voltage mV
10
5
2
1
0,5
0,3
G.B.
distance mm
0,1
0,2
0,3
0,4
0,5
0,6
0,7

Fig.2.

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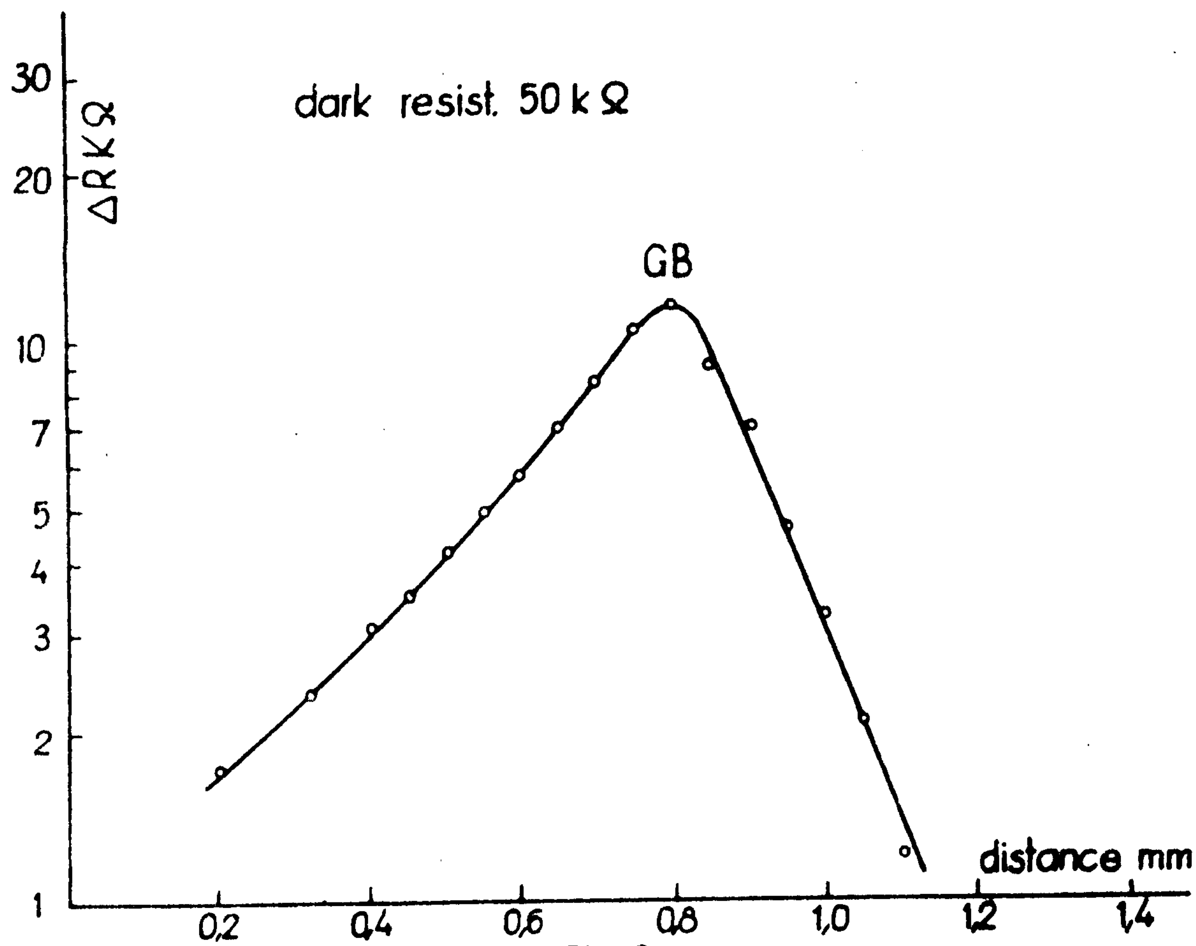

Fig. 3.

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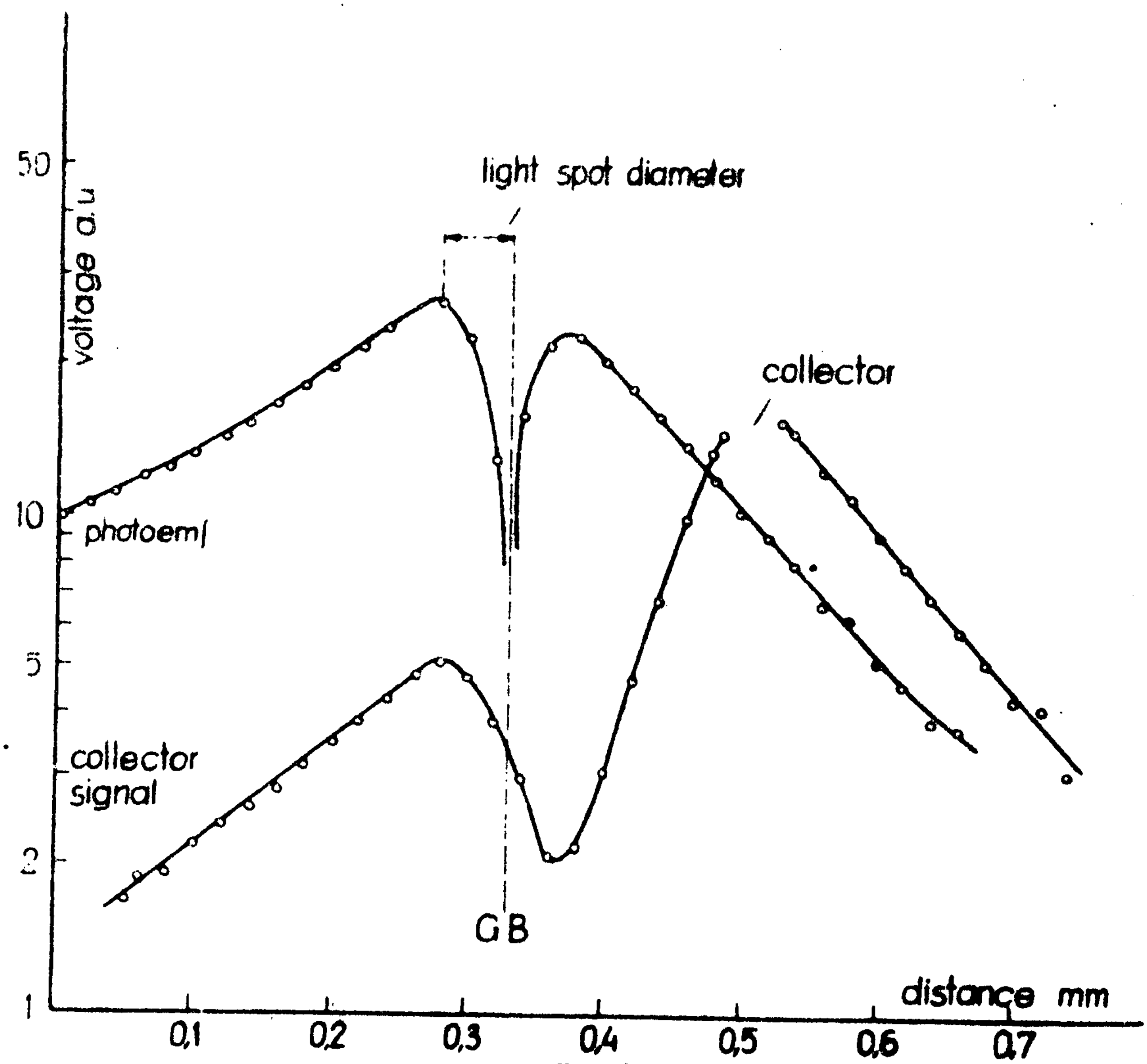

light spot diameter
voltage a.u
50
10
5
2
1
photoemf
collector
collector signal
GB
distance mm
0,1
0,2
0,3
0,4
0,5
0,6
0,7

Fig. 4.

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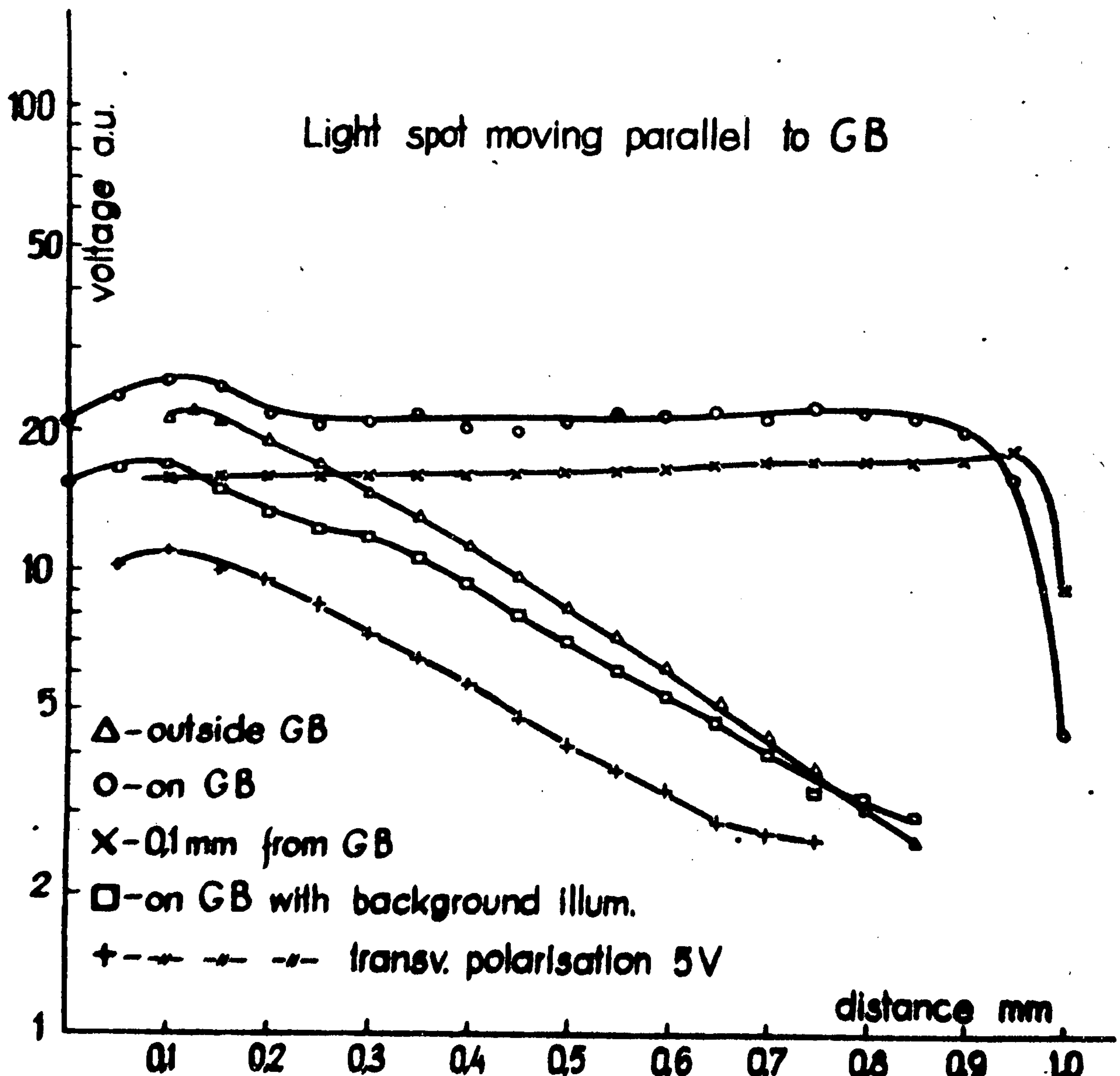

Fig.5.

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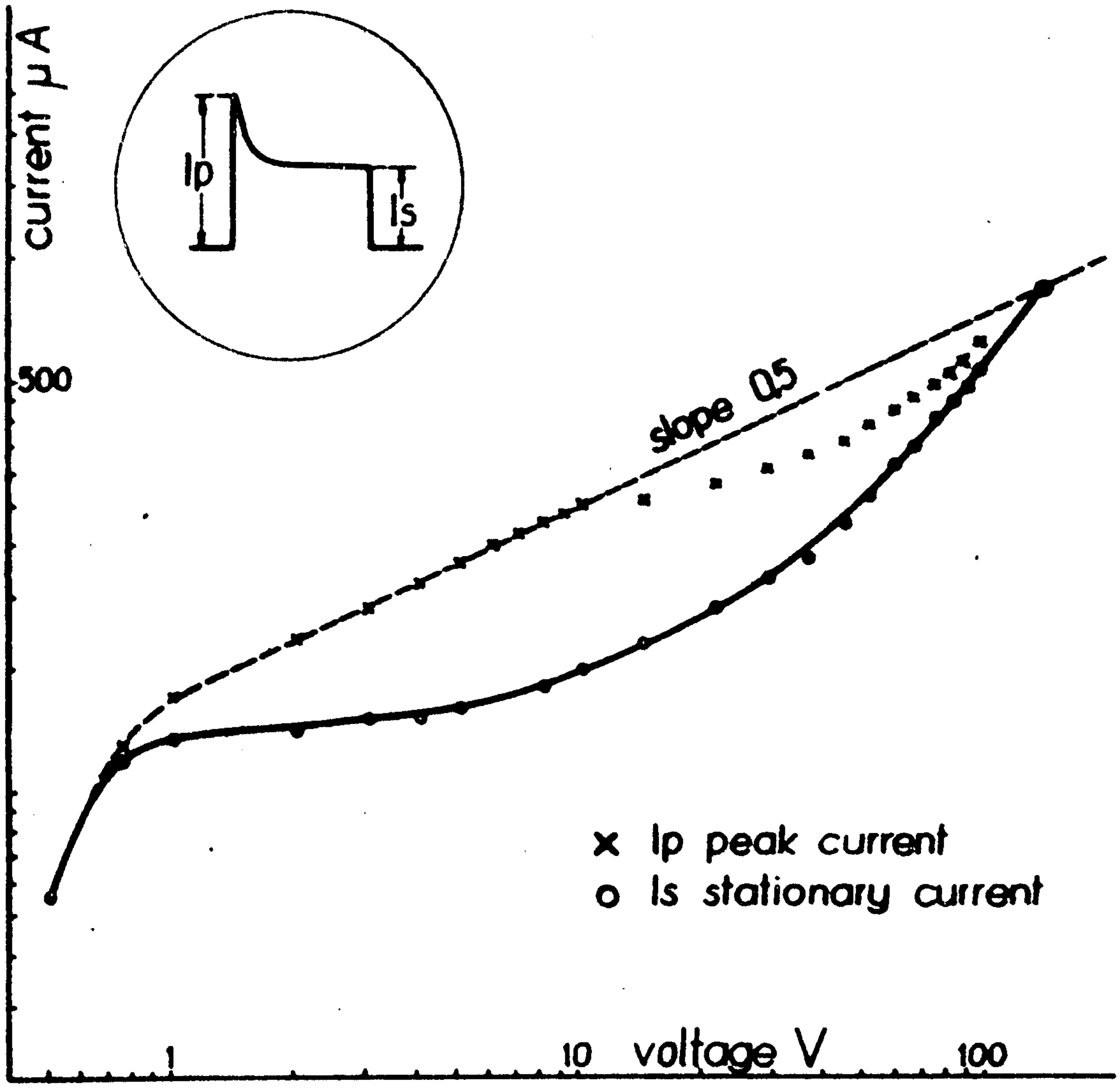
current µA
500
Ip
Is
slope 0.5
× Ip peak current
o Is stationary current
1
10
voltage V
100

Fig. 6.

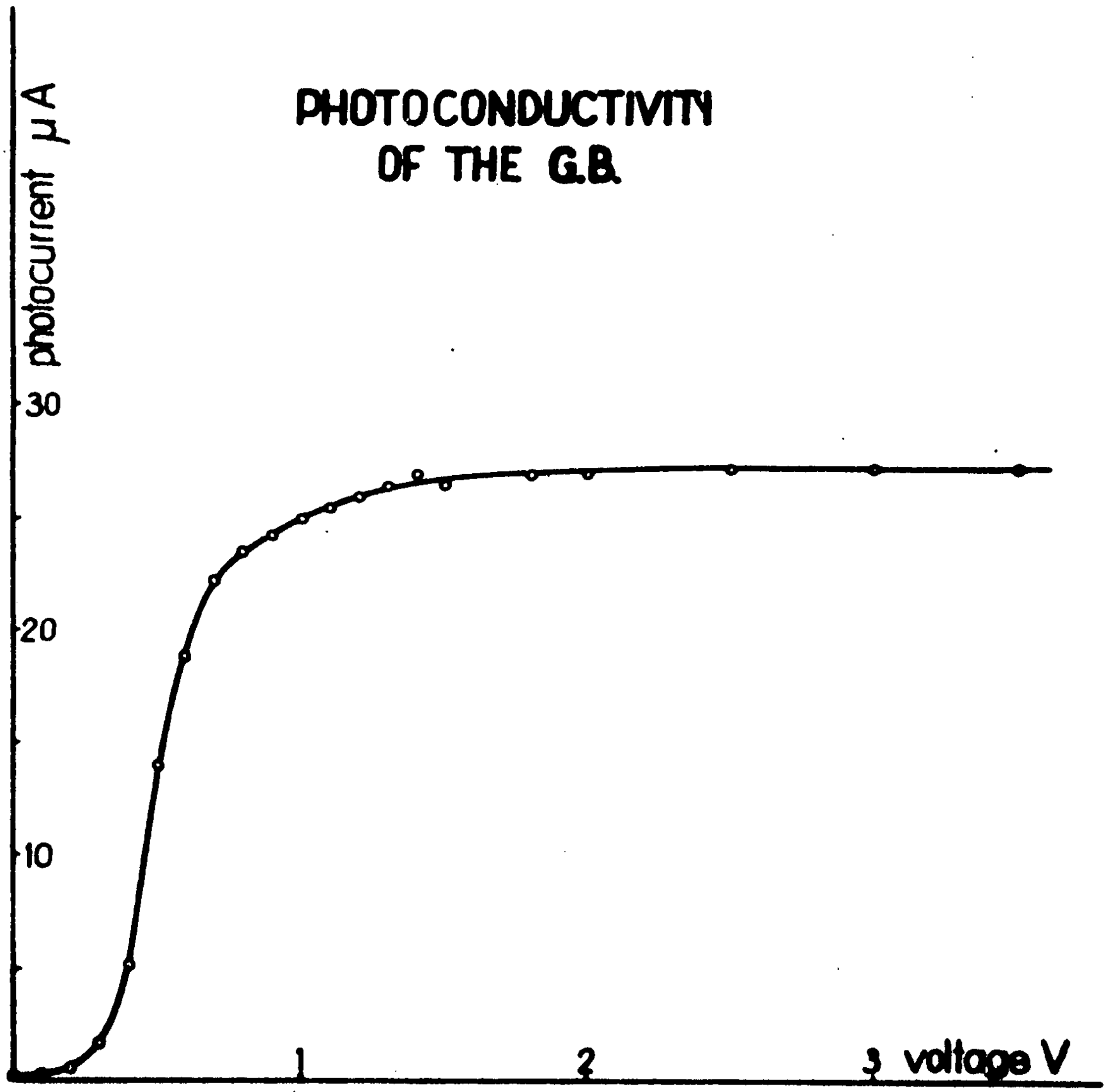
PHOTOCONDUCTIVITY
OF THE G.B.
photocurrent μA
30
20
10
1
2
3
voltage V

Fig.7.